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RECENTLY PUBLISHED RESEARCH OF THE
MILITARY ACADEMY OF CHEMICAL DEFENSE
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"Inductive, Mesomeric and Steric Effects in Unsaturated and Aromatic Acids," A. I. Titov, Lab Org Chem, Mil Acad. of Chem Defense imeni K. E. Voroshilov

"Zhur Obshch Khimi!" Vol 16, 1946, pp 1891-5

The fact that α, β -unsaturated acids are weaker than the corresponding β, γ -unsaturated acids (e.g., $\text{CH}_3\text{CH}=\text{CHCOOH}$, $10^7 K = 1.5$; $\text{CH}_3\text{CH}=\text{CHCOOH}$, $10^7 K = 3.4$) is interpreted by the superposition of a positive mesomeric (+M) effect on the negative inductive (-I) effect, resulting in an increase of the negative charge of the carboxyl and a lessening of the tendency to ionization. The +M effect explains also the increased basic properties of FAME_2 as compared with MeNO_2 , whereas the decrease of the basic properties in FAME_2 , as compared with MeNO_2 is due to the -M effect. The strong increase of acidity from $\text{CH}_3\text{CH}=\text{CHCOOH}$ to $\text{CH}_3\text{C} \equiv \text{CCOOH}$ ($10^7 K = 250$ as against 2.1) is understandable from the fact that the two π -bonds of $\text{C} \equiv \text{C}$ lie in different planes only one of which can be the seat of an M effect, whereas in the other inductive attraction of electrons remains uncompensated. The lowered electrophilism of the carboxyl C, due to the M and the electronegative effects, determines the much lower rates of esterification of α, β -olefin-carboxylic acids in comparison with the corresponding saturated acids, whereas the somewhat greater rate in β, γ -unsaturated acids is explained by the sole occurrence of the I-effect. Inasmuch as full realization of the M-effect of π -bonds depends on

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location of the corresponding atoms in one plane, substituents that disrupt the plane structure on steric grounds will hinder resonance and result in higher acid dissociation; for steric reasons, the cis-forms of $\text{CH}_3\text{CH} : \text{CHCOOH}$ and of $\text{PhCH} : \text{CHCOOH}$ are stronger acids than the trans forms; the same steric factor also underlies the increase of acidity from PhCOOH to $\text{c-MeC}_6\text{H}_4\text{COOH}$ to $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{COOH}$ as contrasted with the acidity-decreasing +I effect of introduction of Me groups in m and p positions. The combined action of the steric and the +I effect is determined for the stability of the $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CO}^+$ carbonium ion in solution in H_2SO_4 .

"Theory of Nitration of Saturated Hydrocarbons and Their Derivatives: I. General Conclusions on the Primary Elementary Stage of the Reaction," A. I. Titov, Lab Org Chem, Mil Acad of Chem Defense imeni K. E. Voroshilov

"Zhur Obshch Khimii" Vol 16, 1946, pp 1896-1906

The ineffectiveness of pure HNO_3 for the nitration of paraffins, paraffinic side chains, and cycloparaffins, was demonstrated in 60-day experiments at room temperature with C_5H_{12} , 2,7-dimethyloctane, cyclohexane, and PhMe, and HNO_3 density 1.40-1.42; results were also negative with C_5H_{12} and cyclohexane at 100° , 10 hours. Nitration proceeds not with HNO_3 but with NO_2 which forms to some extent above 300° ; 50 ml cyclohexane nitrated with HNO_3 (density 1.4) at $320\text{-}40^\circ$ gave only 0.8 g product while the same amount reacting with 12 g NO_2 gave 7.5 g nitrated products. Further proof is derived from experiments on the nitration of PhMe with H_2O_2 with excess of either NO or O_2 . Full details given.

"The Significance of Steric Factors in Alkylation, Acylation, and Related Chemical Reactions," A. I. Titov, Mil Acad of Chem Defense imeni K. E. Voroshilov

"Zhur Obshch Khimii" Vol 16, 1946, pp 2011-18

(1) Velocities of reactions of this type are determined not only by the positive electric charge on the corresponding electrophilic centers but also, to a large extent, by the "coordinative unsaturation" of these centers, expressing the degree of their steric accessibility and their capacity of forming compounds with a higher coordination number without substantially altering the electrical nature of the rest of the molecules; thus, in NO_2 , RCNO , SOCl_2 , the N, C, and S atoms are coordinatively unsaturated and ready to form intermediate complexes without substantial activation. The nucleophilic atom A (charge -c) in the mole. M-X will react faster with either the electrophilic center B_1 or with that at B_2 (charges +a, and +e, steric resistances R_1 and R_2) in the mole (Q) (T) (X) B_1 - B_2 (Y) (Z), depending on the sign of the difference of the driving forces f of the two reactions, approximately equal to the difference

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of the two rate constants: $\Delta K \approx f_1 - f_2 = P(e_1 - e_2) - (R_1 - R_2)$ where P is a function of the distance. (2) These considerations are applied to the reactions of Et_2NH with the nitrite PhCH_2NO_2 (I) and with the nitrate PhCH_2NO_3 (II): 27.4 g I reacted with 60 g Et_2NH under cooling, giving, after 2 days' standing and twice repeated distillation, 94% nitrosodimethylamine, Et_2NNO , boiling at $175-8^\circ$, and 88% PhCH_2OH ; no alkylation took place. On the other hand, 5.8 g II reacted with 10 g Et_2NH with a spontaneous temperature rise to 65° ; solution in 30 ml HCl (1:2), stirring with ether, alkalization, extraction with ether, and distillation of the extract gave 80% $(\text{PhCH}_2)_2\text{Et}_2\text{N}$, boiling at $209-13^\circ$, identical with the product synthesized by boiling on a water bath 5 hours 12.5 g PhCH_2Cl , 25 g Et_2NH , 10 g K_2CO_3 , extraction with 30 ml C_6H_6 , and fractionation (yield 80%); aurate melting at $90-1^\circ$; picrate melting at $121-2^\circ$ (alcohol). The two reactions, acylation by I and alkylation by II, proceed with approximately the same velocity.

"A Study of Highly Concentrated Emulsions of the M/V Type: VII, Stability of Emulsions Protected by Sodium Oleate," A. V. Bromberg, Mil Acad of Chem Defense imeni K. E. Voroshilov

"Kolloidnyy Zhurnal" Vol IX, No 4, 1947, 11 pp

Investigates the process of coalescence in subject emulsions, finding that in emulsions with distended films the volume coalescence in relation to the aging conditions produces either the well-known lowering of the degree of dispersion or partially removes it, but in both cases the adsorption layers become dense to the point of concentration.

"Special Cases of Coloring of Gelatin Layers," K. Chumtsov, G. Yushkevich, Mil Acad of Chem Defense imeni K. E. Voroshilov

"Kolloidnyy Zhurnal" Vol IX, No 4, 1947, 4 pp

Experimental data, with graphs and a diagram of apparatus. Concludes that in case of small concentrations on the edges of a colored zone there is a change of effect: a decrease in density of coloring in the strip, which may be explained by partial washing off of the coloring agent as it begins to collect on the surface of the gelatine but is weakly joined to it.

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